TABLE II

SELECTIVE HYDROGENATION OF ISOPRENE BY BISCYCLOPENTADIENYLVANADIUM DICHLORIDE[a]

Catalyst system	Conversion, %	Content, % 2-Methyl-1-butene	 2-Methyl-2-butene	 2-Methyl-1-butene	 2-Methylbutane
Cp_2VCl_2–BuLi	100.0	5.8	92.1	2.1	0
Cp_2VCl_2–PhMgBr	97.8	4.9	93.7	1.4	0

[a] The hydrogenation reactions were carried out at 95–100° for 15 hr using the catalyst system 2 mmol of Cp_2VCl_2 and 4.8 mmol of BuLi (or 7 mmol of PhMgBr) and 50 ml of benzene as the solvent. The initial hydrogen pressure was 60 kg/cm²; 7 ml of isoprene was used in each experiment.

TABLE III

HYDROGENATION OF BUTADIENE BY MONOCYCLOPENTADIENYL TRANSITION METAL COMPOUNDS[a]

Catalyst system	Conversion, %	Content, % Butene-1	 *cis*-Butene-2	 *trans*-Butene-2	 Butane
$CpNiC_3H_7$–$AlEt_3$	72.7[b]	7.4	30.2	42.3	20.1
$CpNiC_3H_7$–PhMgBr	86.4	0.9	41.2	48.0	9.9
$CpCo(CO)_2$–$AlEt_3$	91.7	0.5	40.5	51.4	7.3
$CpCo(CO)_2$–PhMgBr	87.4	4.7	44.2	48.3	2.8
$CpFe(CO)_2Cl$–$AlEt_3$	98.8	2.1	45.6	52.3	0
$CpFe(CO)_2Cl$–PhMgBr	85.3	1.0	44.7	44.3	0

[a] The hydrogenation reactions were carried out at 40–45° for 6 hr using the catalyst system 2 mmol of $CpNiC_3H_7$, $CpCo(CO)_2$, or $CpFe(CO)_2Cl$ and 4.8 mmol of $AlEt_3$ (or 7 mmol of PhMgBr) and 50 ml of benzene as a solvent. The initial hydrogen pressure was 60 kg/cm²; 7 ml of butadiene was used in each experiment. [b] Cyclooligomerization also occurred.

was contained in the reaction products. On the other hand, in Cp_2VCl_2–BuLi (or PhMgBr) catalyst systems, selective hydrogenation of conjugated diene to monoolefin was observed, and further hydrogenation of monoolefin (butenes) to butane was not observed. In Cp_2ZrCl–BuLi (or PhMgBr) catalyst systems, no hydrogenation reaction was observed. In any case of Cp_2MCl_2 (where M is Ti, V, or Vr)–$AlEt_3$ (or $AlBu_3$) catalysts systems, or in any case of Cp_2M, $Cp_2M^+X^-$ (where M is Ni, Co, or Fe)–organometallic compound (BuLi, PhMgBr, $AlEt_3$, $AlBu_3$) catalyst systems, no hydrogenation reaction was observed.

In Table II, the results of selective hydrogenation of isoprene by Cp_2VCl_2–BuLi (or PhMgBr) catalyst system are shown. The reaction products were 2-methyl-1-butene, 2-methyl-2-butene (main product), and 3-methyl-1-butene. Further hydrogenation of monoolefins to 2-methylbutane was not observed. In Table III, the results of hydrogenation of butadiene by $CpNiC_3H_7$ (or $CpCo(Co)_2$, $CpFe(CO)_2Cl$)–$AlEt_3$ (or PhMgBr) catalysts system are shown. Under the reaction conditions (reaction temperature of 40–45°, reaction time of 6 hr), butene-1 and butene-2 were mainly produced, and butane constituted only a small portion of the reaction products, but by extending the reaction time to 15 hr or using a higher reaction temperature further hydrogenation of butene to butane occurred and the butane content increased.

From the above experimental results, we presume the following: Cp_2TiCl_2 (or Cp_2VrCl_2, Cp_2ZrCl_2) could be alkylated by BuLi (or RMgBr) to form a metal–alkyl bond which could be hydrogenated to yield a metal hydride. Catalytic activity for hydrogenation is mostly dependent on the nature of the center element of the π complex $(T \gg V \gg Zr)$. The π complex of titanium can catalyze the hydrogenation of monoolefins to saturated hydrocarbons, whereas the π complex of vanadium can catalyze the hydrogenation of conjugated dienes to monoolefins, being unable to hydrogenate monoolefins to saturated hydrocarbons. The π complex of zirconium has no catalytic effect on hydrogenation. On the other hand, neither Cp_2M nor $Cp_2M^+X^-$ (where M is Ni, Co or Fe) could be alkylated to form a metal–alkyl bond. These π complexes have no catalytic power on the hydrogenation. By the reaction of $CpNiC_3H_5$ (or $CpCo(CO)_2$, $CpFe(CO)_2Cl$) and $AlEt_3$ (or PhMgBr), a metal–alkyl bond would be formed, which would be followed by hydrogenolysis to yield the metal hydrides. Transition metal compounds of Ni, Co, and Fe themselves can catalyze the hydrogenation of monoolefins to saturated hydrocarbons, but hydrogenation was greatly retarded by coordination from the cyclopentadienyl ligand.

Experimental Section

The hydrogenation reactions were carried out in an autoclave (100 ml), and all opeations were carried out in a nitrogen atmosphere. In general, 2 mmol of a transition metal π complex, 4.8 mmol (or 7 mmol) of an organometallic compound, 50 ml of benzene as solvent, and 7 ml of butadiene (or isoprene) were taken in the autoclave under a nitrogen atmosphere. Hydrogen was then introduced up to 60 kg/cm². The reactions were carried out at 40–45° (or at 95–100°) for 15 hr (or for 6 hr) under strong agitation. The products were analyzed by isolation and were identified or determined by gas chromatography.

Preparation of Transition Metal π Complexes.—Cyclopentadienyldicarbonylcobalt(I), $CpCo(CO)_2$, was prepared[4] by treating a twofold excess of dicobalt octacarbonyl with cyclopentadiene at room temperature. π-Allyl-π-cylopentadienylnickel was prepared[5] by treating Cp_2Ni with allylmagnesium chloride in THF under an inert atmosphere. Cyclopentadienyldicarbonylchloroiron(I)$CpFe(CO)_2Cl$ was prepared[4] by oxidizing cyclopentadienyltetracarbonyliron $(CpFe)_2(CO)_4$ with air in HCl acidic ethanol-chloroform solution.

Cyclopentadienyltetracarbonyliron, $(CpFe)_2(CO)_4$; nickelocene, Cp_2Ni;[6] biscyclopentadienyltitranium dichloride, Cp_2TiCl_2;[7] biscyclopentadienylvanadium dichloride, Cp_2VCl_2; and biscyclopentadienylzirconium dichloride, Cp $ZrCl_2$,[8] were prepared by the procedure as described in the literature.

Registry No.—Cp_2TiCl_2, 1271-19-8; Cp_2VCl_2, 12083-48-6; Cp_2ZrCl_2, 1291-32-3; $Cp_2NiC_3H_7$, 12107-46-9; $CpCo(CO)_2$, 12078-23-8; $CpFe(CO)_2Cl$, 12107-04-9; butadiene, 106-99-0; isoprene, 78-79-5.

(4) T. S. Piper, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(5) W. R. McCallan, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

(6) C. L. Hobbs, British Patent 733,129 (1955).

(7) G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, **76**, 4281 (1934).

(8) G. Wilkinson and F. A. Cotton, *Chem. Ind.* (London), 307 (1954).

Cyclopropanecarboxylic Acid Fluoride. An Improved Synthesis

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Cyclopropanecarboxylic acid fluoride was reported previously[1] to be obtained in 30% yield by the action of potassium fluoride on cyclopropanecarboxylic acid chloride and in 54% yield by allowing the free acid to

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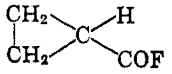
(1) M. Hanack and H. Eggensperger, *Chem. Ber.*, **96**, 1341 (1963).

react with a mixture of benzoyl chloride and potassium fluoride.

We have found that, when 4-chlorobutyryl chloride is treated with potassium fluoride at 195–200° in a suitable reaction medium such as tetramethylene sulfone, cyclopropanecarboxylic acid fluoride is produced directly in 70% yield (eq 1). Since 4-chlorobutyryl

$Cl(CH_2)_3COCl + 3KF \rightarrow$



$+ KHF_2 + 2KCl$ (1)

chloride is easily made from γ-butyrolactone and thionyl chloride,[2a,b] this approach appears to offer a practical route to the acyl fluoride and its many derivatives.

We have evidence to show that the reaction proceeds in two distinct steps which, at the optimum elevated temperature, are practically concerted. First there is an exothermic exchange of the acyl halogen atom, followed by a base-induced cyclization, to give the product observed.

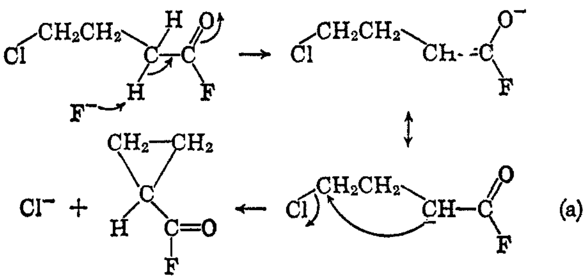
The first step in the reaction is the exchange of the acyl halogen for fluorine. This was demonstrated by running the reaction at various temperatures. At 130° the sole product is 4-chlorobutyryl fluoride. This product may be recovered and distilled or, simply by raising the temperature in the reaction flask to 190–195°, it may be converted into cyclopropanecarboxylic acid fluoride. Below 190° no cyclic product was observed. It was further noted that, when 4-chlorobutyryl chloride was added to the potassium fluoride–tetramethylene sulfone slurry, an exothermic reaction took place, resulting in a temperature rise of about 10° in the reaction flask. As no similar increase in temperature occured when the acid chloride was mixed with the sulfone alone, the results noted above must be due to the initial exchange reaction.

Whereas halogen exchange reactions brought about by potassium fluoride are well known,[3,4] its use as a base has been more limited. The basic properties of potassium fluoride were noted first in 1948[5] by Nesmayanov and his colleagues, who discovered that the reaction in eq 2 did not proceed as anticipated. Instead, a base-induced decarboxylation was observed, with the formation of chloroform and carbon dioxide.

$$CCl_3COOH + 3KF \not\rightarrow CF_3COOH + 3KCl \qquad (2)$$

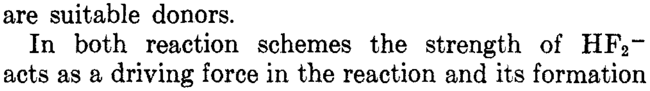
Prior to this, it was thought that more powerful nucleophiles, such as amines or hydroxides, were required for this type of reaction. Further examples of the use of potassium fluoride as a base have been summarized recently.[6] The second stage of the reaction, then, may be written simply as the abstraction of an α proton, followed by an intramolecular nucleophilic displacement, resulting in ring closure (see Scheme I).

SCHEME I



$$HF + KF \rightarrow KHF_2 \qquad \text{(b)}$$

It has been suggested[7] that potassium fluoride is not a strong enough nucleophile to react with an α-hydrogen atom, *e.g.*, in adipic acid, but this reasoning may not apply here because the α hydrogen is rendered relatively acidic by the acyl fluorine atom. The importance of the acyl fluorine atom is shown by the fact that efforts to cyclize 4-chlorobutyronitrile, 4-chlorobutyranilide, and ethyl 4-chlorobutyrate by heating with potassium fluoride were unsuccessful. It is interesting to note that 4-chlorobutyronitrile can be cyclized by heating with sodium hydroxide[8] and that a mixture of ethyl 4-iodobutyrates gives good yields of ethyl cyclopropanecarboxylate[9] when heated with sodium hydride, indicating that very strong bases are required in the absence of the unique activating influence present in the acyl fluoride. It is also possible that initially there is formed a strong hydrogen bond (see eq 3) followed by formation of KHF_2 and a carbanion. The incipient carbanion in both cases would have resonance stabilization through the enolate form, and could subsequently cyclize. Fluoride ions are capable of forming the strongest known hydrogen bonds,[10] *i.e.*, F^- acting as a Lewis base and it has been shown[11,12] that active methylene compounds are suitable donors.



$$H{-}\overset{|}{\underset{|}{C}}{-}H + KF \rightleftarrows H{-}C^- + \bar{H}\cdots\cdots FK \overset{F^-}{\rightleftarrows} H{-}C^- + KHF_2 \qquad (3)$$

In both reaction schemes the strength of HF_2^- acts as a driving force in the reaction and its formation ties up excess acid, to which the product is sensitive.[13]

In a brief examination of the ability of other alkali metal fluorides to bring about the cyclization, we carried out the reaction with cesium fluoride and with sodium fluoride. The former, as expected, gave the cyclopropanecarboxylic acid fluoride, but only in the same yield (70%) as potassium fluoride. Sodium

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(2) (a) W. Reppe, *Ann. Chem.*, **596**, 1 (1955). (b) $Cl(CH_2)_3COCl$ is also available from Aldrich Chemical Co.

(3) M. Hudlický, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962, p 87 ff.

(4) A. K. Barbour, L. J. Belf, and M. W. Buxton, *Advan. Fluorine Chem.*, **3**, 181 (1963).

(5) A. N. Nesmayanov, K. A. Pecherskaya, and G. Y. Uretskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 240 (1948).

(6) L. Rand, D. Haidukewych, and R. J. Dolinski, *J. Org. Chem.*, **31**, 1272 (1966).

(7) L. Rand, W. Wagner, P. O. Warner, and L. R. Kovac, *ibid.*, **27**, 1034 (1962).

(8) C. M. McCloskey and G. H. Coleman in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 221.

(9) B. W. Horrom and L. R. Swett (Abbott Laboratories), U. S. Patent 2,992,269(July 11, 1961).

(10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 460.

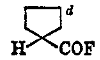
(11) A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 1233, 1715 (1963).

(12) E. LeGoff, *ibid.*, **84**, 3975 (1962).

(13) If the crude product is left to stand overnight it decomposes to a certain extent. This is thought to be due to traces of HF carried over by the product. Although the decomposition temperature of KHF_2 is given as 225°, it is an equilibrium and probably occurs to a limited extent at 200°.

TABLE I

PREPARATION OF CYCLOPROPANECARBOXYLIC ACID FLUORIDE AND 4-CHLOROBUTYRYL FLUORIDE[a]

Acyl halide	Mole ratio KF/acyl halide	Reaction medium[b]	Reaction temperature, °C	Product (yield, %)
$Cl(CH_2)_3COCl$	3.86	T	195–200	$\overline{CH_2CH_2CHC}OF$ (70)
$Cl(CH_2)_3COCl$	2.44	T	195–200	$\overline{CH_2CH_2CHC}OF$ (70)
$Cl(CH_2)_3COCl$	2.44	N	195–200	$\overline{CH_2CH_2CHC}OF$
$Cl(CH_2)_3COCl$	1.94	T	195–200	$\overline{CH_2CH_2CHC}OF$ (37) + $Cl(CH_2)_3COF$
$Cl(CH_2)_3COCl$	2.44	T	130–140	$Cl(CH_2)_3COF$ (52)
$Cl(CH_2)_3COCl$	4.14[c]	T	197	$Cl(CH_2)_3COF$ (40)
$Br(CH_2)_3COCl$	6.36	N	195–200	$\overline{CH_2CH_2CHC}OF$ (23)
$Cl(CH_2)_4COCl$	2.69	T	195–200	Not identified
$Br(CH_2)_5COCl$	3.66	T	195–200	 H COF [d] $CH_2{=}CH(CH_2)_3COF$ $F(CH_2)_5COF$

[a] The low boiling products were distilled from the reaction vessel as they were formed. Where the products were removed by vacuum distillation, a prior reaction time of 1–2 hr was used. [b] T = tetramethylene sulfone; N = N-methylpyrrolidone. [c] NaF. [d] Identified by infrared and nmr spectroscopy and by preparation of the amide, mp 177–178°.

fluoride gave only 4-chlorobutyryl fluoride. This latter result would be expected upon consideration of the base strengths of the alkali metal fluorides.[14]

The scope of the reaction is further illustrated by the conversion of 4-bromobutyryl chloride into cyclopropanecarboxylic acid fluoride and by the use of various "solvents" for the potassium fluoride. We find that tetramethylene sulfone, N-methylpyrrolidone and γ-butyrolactone give satisfactory results, although the first is preferred chiefly because its higher boiling point minimizes contamination of the product. Dimethyl sulfone can be used, but its high melting point (109°) is a serious drawback. When nitrobenzene is the reaction medium, even at temperatures up to 210°, the major product is the open chain chlorobutyryl fluoride, with only minor amounts of the cyclic compound. Therefore, the solubility of the metal fluoride in the reaction medium appears to be an important factor.

Apparently the reaction is limited to 4-halobutyryl halides, since higher homologs do not cyclize readily. Thus, 5-chlorovaleryl chloride did not give any cyclobutanecarboxylic acid fluoride and 6-bromohexanoyl chloride gave, in low yield, a mixture of three products, from which a small amount of cyclopentanecarboxylic acid fluoride could be distilled. The other products were 6-fluorohexanoyl fluoride and 5-hexenoyl fluoride. These results suggest that thermodynamic and energy factors govern the course of the reaction.

Experimental Section

Representative procedures for the preparation of cyclopropanecarboxylic acid fluoride and 4-chlorobutyryl fluoride are given below. The results of other experiments are given in Table I. Tetramethylene sulfone was practical grade, supplied by Distillation Products Industries. Potassium fluoride was Baker and Adamson (2091), finely ground and dried at 160–170°. 4-Bromobutyryl chloride was purchased from K & K labs; all other reagents were obtained from Aldrich Chemial Company.

Cyclopropanecarboxylic Acid Fluroide.—A 2-l. three-necked, creased flask (Morton type) was fitted with a dropping funnel, thermometer, take-off head with condenser, and a high-speed blade stirrer. Tetramethylene sulfone (500 ml) was placed in the flask and the temperature raised to 195–200°. Dry potassium fluoride (159 g, 2.74 mol) was added and followed, with vigorous stirring, by 4-chlorobutyryl chloride (100 g, 0.71 mol). The rate of addition of the acyl chloride was adjusted so that the temperature in the take-off head was maintained between 80 and 100°. The temperature in the reaction flask rose rapidly to 209° and, after a few minutes, a colorless distillate began to collect. Total addition of the acyl chloride took 50 min. The crude product which had collected was distilled through a 6-in. Vigreux column to give cyclopropanecarboxylic acid fluoride (44 g, 70.4% of theory): bp 81°; $n^{25}D$ 1.3775. The infrared spectrum of the neat liquid showed a strong C=O stretching band at 1842 cm^{-1}. Hanack[1] reports bp 80–81° and C=O stretching at 1840 cm^{-1}. The 60-MHz pmr spectrum showed two complex multiplets, that of the α proton being centered at δ 1.70 ppm from tetramethylsilane. The β protons were less deshielded and appeared at 1.11 ppm. The integrated areas under the multiplets were 1:4.

4-Chlorobutyryl Fluoride.—In a similar manner 100 g (0.71 mol) of 4-chlorobutyryl chloride was treated with 100 g (1.73 mol) of potassium fluoride in tetramethylene sulfone at 130°. An exothermic reaction took place and the temperature rose to 139°. After the addition of the acyl chloride had been completed, the temperature reverted to 130°. The mixture was stirred vigorously for 2 hr, but no distillate collected despite the aid of a nitrogen sweep. The pressure in the system was reduced to about 150 mm, while still maintaining a temperature of 130°. A colorless product was collected, which was redistilled to give 47 g of 4-chlorobutyryl fluoride, bp 60° (100 mm) or 137–139°. Its infrared spectra also had a strong C=O stretching band at 1842 cm^{-1}. The 60-MHz pmr spectrum showed three multiplets: $-CH_2Cl$ at 3.70 ppm from tetramethylsilane, appeared as a triplet, with some unresolved fine structure (J_{HCCH} = 6.5 Hz); $-CH_2COF$ at 2.77 ppm was also a triplet with fine structure (J_{HCCH} = 6.5 Hz); $-CH_2-$ appeared as a pentet with fine structure at 2.16 ppm (J_{HCCH} = 6.5 Hz).

Registry No.—Cyclopropanecarboxylic acid fluoride, 694-02-0; 4-chlorobutyryl fluoride, 15973-66-7.

Acknowledgment.—We are grateful to Professor Jerrold Meinwald for helpful discussions and to Dr. B. B. Stewart and Mr. R. J. Tepper for assistance with the nmr spectra.

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[14] L. Rand, J. V. Swisher, and C. J. Cronin, *J. Org. Chem.*, **27**, 3505 (1962).